

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Art Unit : 1745  
Examiner :  
Serial No. : 10,045,848  
Filed : November 7, 2001  
Inventors : Hiroki Nakamaru



22469

: Tomoshige Ono  
: Yoshiei Kato  
Title : IRON POWDER FOR  
: REMEDIATION AND METHOD  
: FOR REMEDIATING SOIL,  
: WATER OR GAS

Confirmation No: 2392

Docket: 1315-01

**DECLARATION**

I, I. DANIEL CHRISTENBURY, am a resident of 1111 Lanark Road, Centerville, DE 19807. I am a principal in the firm of Schnader Harrison Segal & Lewis. I am admitted to practice in the States of Virginia and Pennsylvania and am registered to practice before the U.S. Patent and Trademark Office.

The entire complete application, including pages 2, 3, 13, 17 and 19 of the Specification, was deposited in the U.S. Post Office via Express Mail, Certificate No.: EL864966362US for delivery to the United States Patent and Trademark Office under date of November 7, 2001.

I personally checked each page of the entire application and found them all to be present in their entirety and in the correct order, which included aforementioned pages 2, 3, 13, 17 and 19 prior to mailing. This is in accordance with my established regular practice of checking each page of the specification for every application I file in the U.S. Patent and Trademark Office.

I then signed the application papers which were, at that point, placed directly into an Express Mail Envelope and sealed, without disturbing any of the application pages, without removing any of the application papers or disturbing their order. This is possible by virtue of the fact that the file copies and client copies of the Application are made prior to the final checking of the application and determination that all of the application pages are present and in the correct order.

The undersigned declares that all statements made herein of his own knowledge are

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**DECLARATION**

I, GINOLA L. JOHNSON, am a resident of 338 Cobble Creek Curve, Newark, DE 19702. I am a secretary in the firm of Schnader Harrison Segal & Lewis.

The entire complete application, including pages 2, 3, 13, 17 and 19 of the Specification, was deposited in the U.S. Post Office via Express Mail, Certificate No.: EL8649663621 S for delivery to the United States Patent and Trademark Office under date of November 7, 2001.

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New U.S. Application for Hiroki Nakamura et al entitled IRON POWDER  
REMEDIATION AND METHOD FOR REMEDIATING SOIL WITH  
GAS

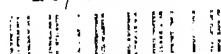
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J. Daniel Christenbury

[0007] However, in the vapor extraction methods, the pump-and-treat methods and the like, facilities must be separately provided at the site to render the pollutants harmless after the aforementioned drawing or pumping. Therefore, the treatment cost is increased.

[0008] In the methods in which the excavated soil is thermally destructed at high temperatures and the like, a large-scale facility is required for the heat treatment of the soil. Furthermore, since soil particles themselves deteriorate due to heat and functions of, for example, growing living organisms, which are inherent in the soil, are substantially degraded, it is difficult to reuse the soil after the treatment.

[0009] The bioremediation method cannot be applied to all soil because the soil at each site has different characteristics. Even when it is applied, reactions proceed slowly since they rely on the function of microbes and the method requires a long treatment time and, therefore, has poor usefulness in practice.

[0010] As a method which might overcome the aforementioned problems of conventional measures against the pollutants, various methods, in which halogenated hydrocarbons as pollutants are contacted with iron functioning as a reducing agent to render them harmless by dehalogenation, have been suggested and have attracted attention.

[0011] For example, Japanese Unexamined Patent Application Publication (Tokaihyo) No. 5-501520 (WO 91/08170) describes a method in which a channel is dug in a flow path of groundwater and filled with iron in the form of particles, slices, fibers, or the like.

Subsequently, the iron is contacted with the halogenated hydrocarbons which cause pollution of the groundwater to dehalogenate and render the halogenated hydrocarbons harmless. The iron used in that process is not necessarily specifically prepared and, therefore, generates waste after the use. In cutting materials, long-persistent powders such as iron powder are generated during the steps of cutting iron and the like.

[0012] A method similar to the aforementioned method in which halogenated

hydrocarbons contained in the groundwater as pollutants are rendered harmless by using metal iron mixed with activated carbon, is described in Japanese Unexamined Patent Application Publication (Tokaihyo) No. 6-507931 (WO 02/19556).

[0013] Japanese Unexamined Patent Application Publication (Tokaihyo) No. 11-235577 discloses a method in which chlorinated organic compounds contained in the soil above the level of groundwater or the excavated soil is contacted with an iron powder and rendered harmless by dechlorination. The iron powder used in this method must have a C content of 0.1% or more and a specific surface area of 0.05 m<sup>2</sup>/g or more. Further, this iron powder must have such a particle size that 50% by weight or more of the iron powder passes through sieve openings of 150µm. A spongy iron ore reduced iron powder has been recommended for such an iron powder.

[0014] International Patent Publication WO 97/04868 describes a method in which a mixed metal produced by precipitating at least one metal selected from the group consisting of Cu, Co, Ni, Mo, Bi, Sn, Pb, Ag, Cr, Pd, Pt and Au on an iron powder is contacted with an aqueous composition polluted with halogenated hydrocarbons, and the halogenated hydrocarbons are dehalogenated and, therefore, the aqueous composition is remedied.

[0015] Each of the aforementioned methods, in which halogenated hydrocarbons as pollutants are contacted with iron, functioning as a reducing agent and rendered harmless by dehalogenation, has a certain advantage and, therefore, is superior to conventional measures against the polluted soil and the polluted groundwater.

[0016] However, the iron used in the aforementioned methods may not be optimized for the aforementioned purposes and uses and, therefore, there has been a problem in that halogenated hydrocarbons cannot always be destroyed at a sufficient speed.

[0017] On the other hand, the method disclosed in International Patent Publication No. 06/76009 is intended to improve the speed of dehalogenation of the halogenated

The media's slowness here may be acidic or alkaline. The pH of the media's oil is preferably within 1 to 10. When groundwater is remediated, the concentration of dissolved oxygen in the groundwater is not specifically limited and, therefore, the invention can be applied over a wide range.

- 5 [0058] The halogenated hydrocarbons contained in the media's oil, water, and gas undergo a dehalogenation reaction by contact with the iron powder for remediation according to the invention, and are decomposed into harmless compounds containing no halogen elements and hydrogen halides. For example, TCH receives an electron (be reduced) from the surface of the iron powder, and forms an unstable intermediate, for example, chloroacetylene, by  $\beta$  elimination. Furthermore, the resulting intermediate is decomposed into compounds not containing chlorine, for example, acetylene. Sometimes, further reactions occur, although at all events, the dehalogenation reaction proceeds by the reception of the electron (be reduced) from the surface of the iron powder and, as a result, decomposition into harmless compounds proceeds.
- 10 [0059] (Examples)

The invention will be described below using Examples, although the invention is not limited to these.

#### (Examples 1 to 6)

##### (1) Preparation of iron powder for dehalogenation

- 20 [0060] An as atomized powder was produced from a molten steel at 1700 °C by a water atomization process. Subsequently, reduction was performed in a stream of hydrogen at 900 °C for 1 hour, and then, pulverization and adjustment of particle diameter were performed. The components in the iron powder at this stage were examined, the result that the contents of the primary components, that is, iron and carbon in the iron powder, are as shown in Table 1.

Table 11

Sample	Iron powder for remediation Particle diameter (amount of powder passed through 75 $\mu\text{m}$ sieve) (% by mass)	Metal compound covering rate <sup>1)</sup> (% by area)	Halogenated hydrocarbon destruction test	
			Soil	Groundwater
Example 1	60% by mass or more	TiN 5	0.05	0.06
2	60% by mass or more	TiN 10	0.01	0.02
3	60% by mass or more	TiN 30	0.02	0.01
4	60% by mass or more	TiN 60	0.10	0.50
Comparative example 1	60% by mass or more	0	0.99	0.98
Example 5	60% by mass or more	TiO <sub>2</sub> 5	0.20	0.30
6	60% by mass or more	TiO <sub>2</sub> 10	0.03	0.05
7	60% by mass or more	TiO <sub>2</sub> 30	0.02	0.03
8	60% by mass or more	TiO <sub>2</sub> 60	0.70	0.80
Comparative example 2	60% by mass or more	TiO <sub>2</sub> 10	0.97	0.98

1) Ratio of TCE concentration of sample to TCE concentration of reference sample after test for 3 days

- 2) Electric resistivity    TiN  $2.17 \times 10^{-3} \Omega \cdot \text{m}$   
                                   TiO<sub>2</sub>  $3 \times 10^{-3} \Omega \cdot \text{m}$   
                                   TiO<sub>2</sub>  $1.2 \times 10^{-3} \Omega \cdot \text{m}$

(Examples 9 to 12)

[0071] An iron powder for remediation was prepared in a manner similar to those in Examples 1 to 4 by using a  $\text{V}_2\text{O}_5$  powder (electric resistivity  $1 \times 10^{-3} \Omega \cdot \text{m}$ ) instead of the TiN powder, and the destruction test of the halogenated hydrocarbons in the soil and the destruction test of trichloroethylene in the groundwater were carried out. The results are shown in Table 2.

destruction test of the halogenated hydrocarbons in the groundwater were carried out in a manner similar to that in Example 1. The results of the destruction tests and measurements are shown in Table 1.

(Comparative example 2)

- 5 [0074] An iron powder having a  $\text{TiO}_2$  powder covering rate of 10% by area was prepared using a  $\text{TiO}_2$  powder (electric resistivity  $\rho = 1.2 \times 10^6 \Omega \cdot \text{m}$ ) having an electric resistivity greater than  $1 \times 10^6 \Omega \cdot \text{m}$  instead of the TiN powder. Thereafter, the destruction test of the halogenated hydrocarbons in the soil and the destruction test of the halogenated hydrocarbons in the groundwater were carried out in a manner similar to that in Example 1. The results of the destruction tests and measurements are shown in Table 1.

- 10 [0075] When the inorganic compound is not present on the iron powder (Comparative example 1), or the inorganic compound ( $\text{TiO}_2$ ) having an electric resistivity greater than about  $1 \times 10^6 \Omega \cdot \text{m}$  is present on the iron powder (Comparative example 2), the speed of destruction is low and, therefore, the trichloroethylene concentrations are hardly decreased after testing for 8 days. On the other hand, decreases in the concentration are clearly observed when an inorganic compound having an electric resistivity of about  $1 \times 10^6 \Omega \cdot \text{m}$  or less (TiN: electric resistivity  $\rho = 2.17 \times 10^4 \Omega \cdot \text{m}$ ,  $\text{TiO}_2$ : electric resistivity  $\rho = 3 \times 10^6 \Omega \cdot \text{m}$ , or  $\text{V}_2\text{O}_5$ : electric resistivity  $\rho = 1 \times 10^5 \Omega \cdot \text{m}$ ) is present on the iron powder for remediation according to the invention (Examples 1 to 12).

- 20 [0076] The iron powder for remediation according to the invention has an unexpectedly and remarkably increased degradation speed of halogenated hydrocarbons. There is no fear of the problem of secondary pollution due to metals contained in the iron powder, and the iron powder of the invention can be inexpensively produced. Furthermore, the iron powder of the invention can be applied to conventional methods in which iron powder is used to render the polluted soil permeable and the like, thereby halogenated